NASA Failure Investigation of High Energy Li-Ion Cell Build by Full Cell Pouch Cell with Reference Electrode Assessment and in Combination with Destructive Physical Analysis

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Outline

- Introduction/Background
- NASA High Energy Cell Build Failure
- Approaches to Failure Investigation
- Summary of Results
- Recommendation/Next Steps

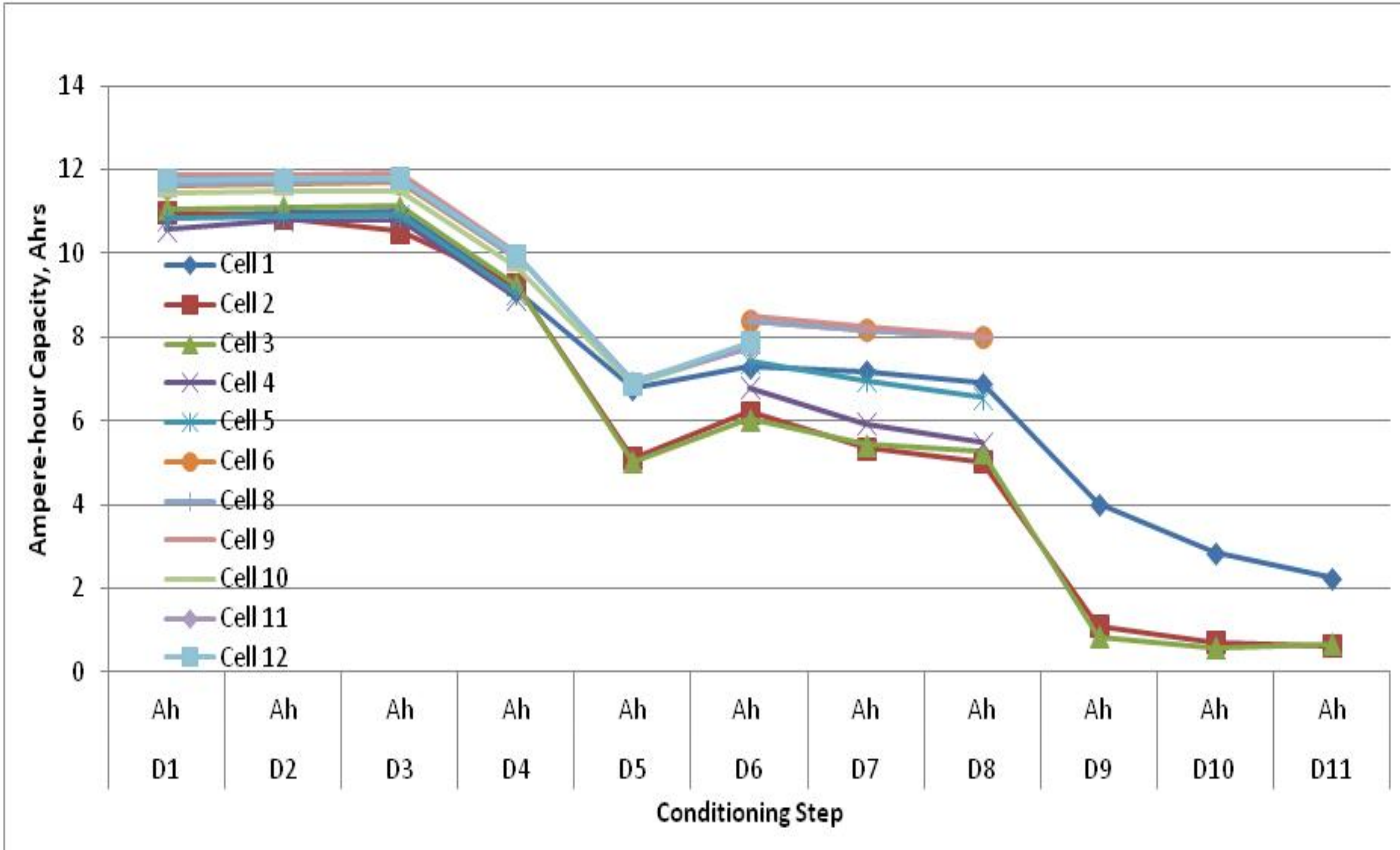
NASA: High Energy (HE)/Ultra High Energy (UHE) Li-ion Cell Development

- NASA is developing High Energy (HE) and Ultra-High Energy (UHE) Li-ion cell designs and batteries for future exploration missions

	High Energy (HE)	Ultra High Energy (UHE)
Anode	Conventional Graphite (MPG 111)	Developmental Nano Si anode (by GeorgiaTech)
Cathode	Li-rich NMC (Toda 9100)	Developmental Li-rich NMC (by UT-Austin)
Electrolyte	Baseline Electrolyte	Developmental Fire-retarded electrolyte (by JPL)
Projection of Energy Density (Wh/kg) (specific on 18650 cell, C/10 10^{o}C)	200	265

- The development of UHE Li-ion cells and batteries will be the main focus

The Initial NASA High Energy (HE) Cell Build Failed



Approach for Failure Investigation at NASA GRC

- Assessment using full cell pouch cell configuration with reference electrode
    - Harvested anode, cathode and separator from remaining but non-activated cells (i.e. dry cells, no electrolyte was added)
    - Fabricated pouch cells using the harvested anode, cathode separator, with a reference electrode (Li metal) inserted between
    - Added the same type of electrolyte and quantity of electrolyte equivalent to actual cell build (40% access based on the porosity)
    - Adapted the same formation and test protocol for the pouch cell as actual cells

- Impedance monitoring before and after formation and at cycling stages (non-destructive analysis)
    - Whole cell
    - Anode vs. reference electrode
    - Cathode vs. reference electrode

- Destructive Physical Analysis (DPA)
    - SEM/EDX
    - ICP/Mass Spectroscopy

What We Learned from Harvested Components: Originally Intended Separator Was Not Used

- The initial observation of delayed wetting of electrolyte on harvested separator – suspecting wrong type of separator was used

- SEM/FT-IR analysis further confirmed that incorrect type of separator was used

- The harvested separator (Celgard 25 μm): multi-layer and thicker

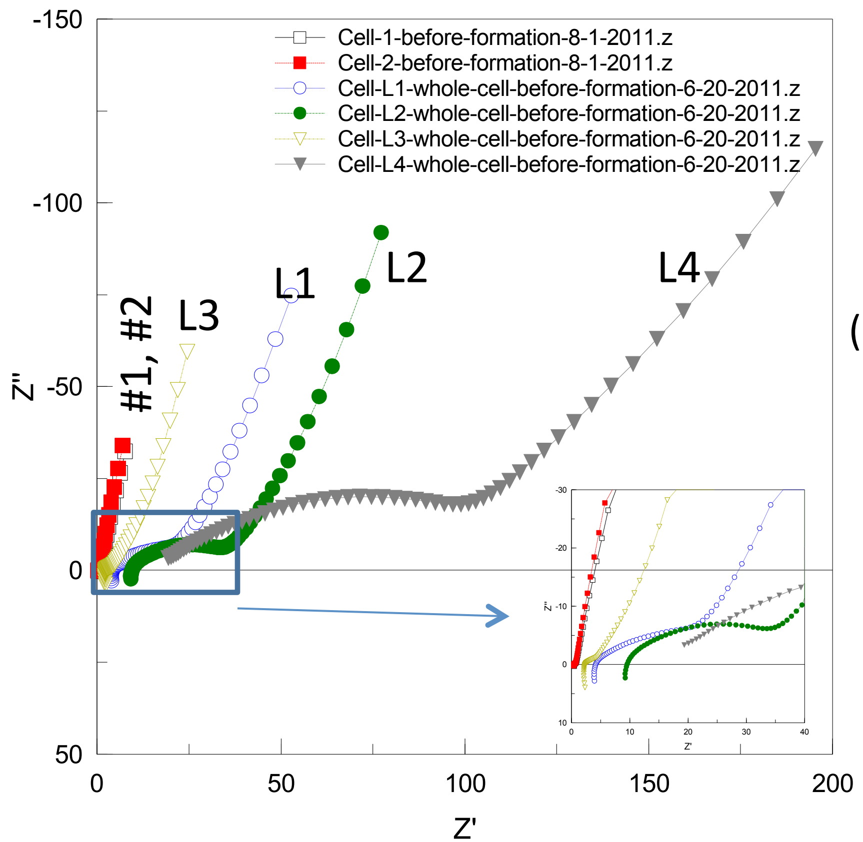
- The original intended separator (Tonen 16 μm): single layer and thinner

Pouch Cell Full Cell: Matrix for Failure Investigation

	Separator	Electrolyte		Anode	Cathode
		Quantity	Type		
Group 1 (cell#: L2, L4)	Harvested (Celgard 25µm)	Limited, 40% access (equivalent to used in actual cell) (0.178ml)	same as used in actual cell (baseline electrolyte)	MPG 111 (harvested)	Toda 9100 (harvested)
Group 2 (Cell#: L1, L3)	originally Intended (Tonen 16 µm)	Limited, 40% access (equivalent to used in actual cell) (0.178ml)			
Group 3 (Cell#: 1,2)	originally Intended (Tonen 16 µm)	Flooded (1.5 ml)			

The anode, cathode and separator were harvested from the same failed lot but non-activated cells

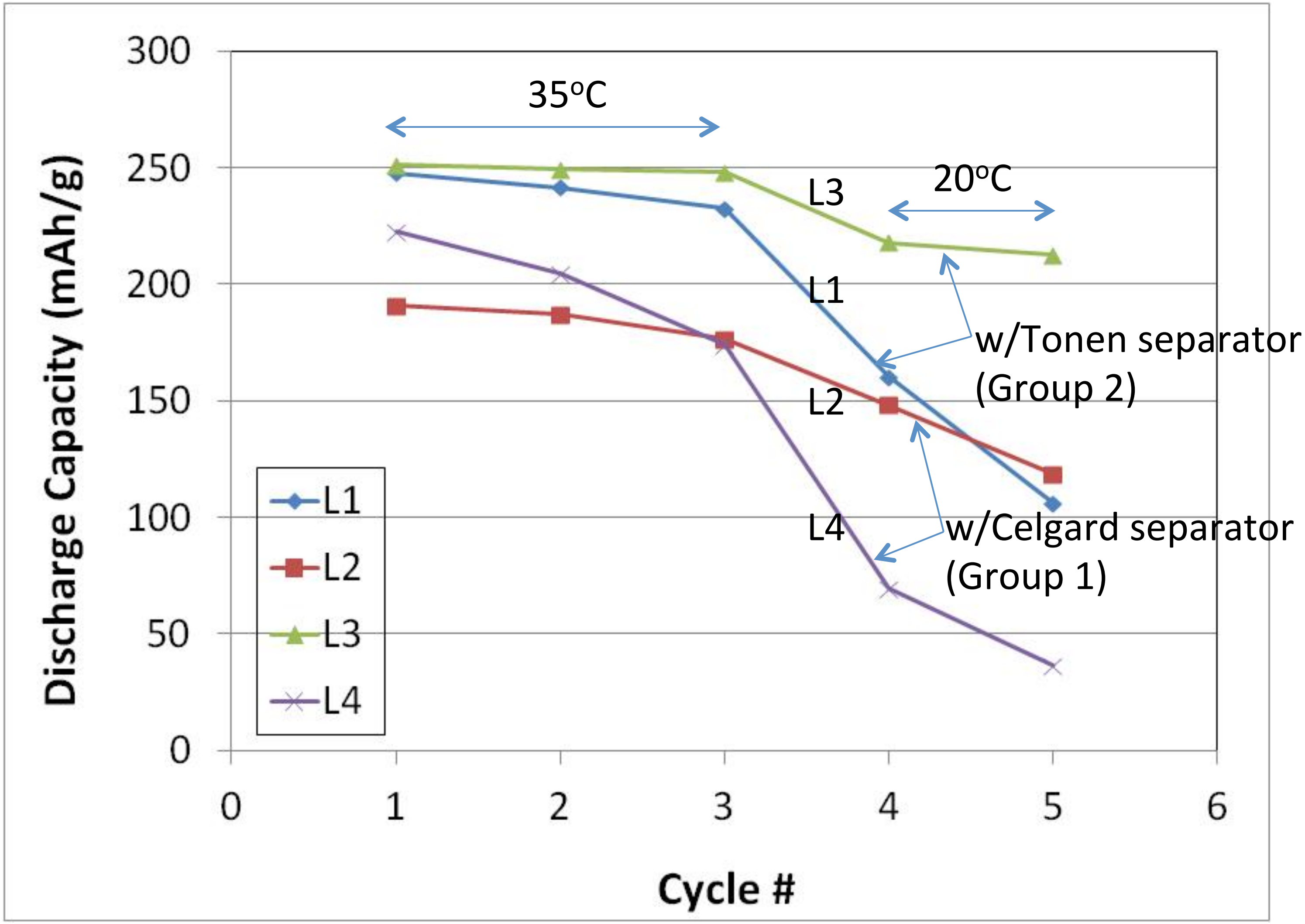
Initial Impedance Measurement: Before Formation



	Cell#	Rs (Ω)	Rct (Ω)
Group 1 (Celgard, limited)	L2	9.34	31.76
	L4	14.63	123.54
Group 2 (Tonen, limited)	L1	4.50	18.10
	L3	2.37	3.72
Group 3 (Tonen, flooded)	#1	0.47	0.77
	#2	0.43	0.82

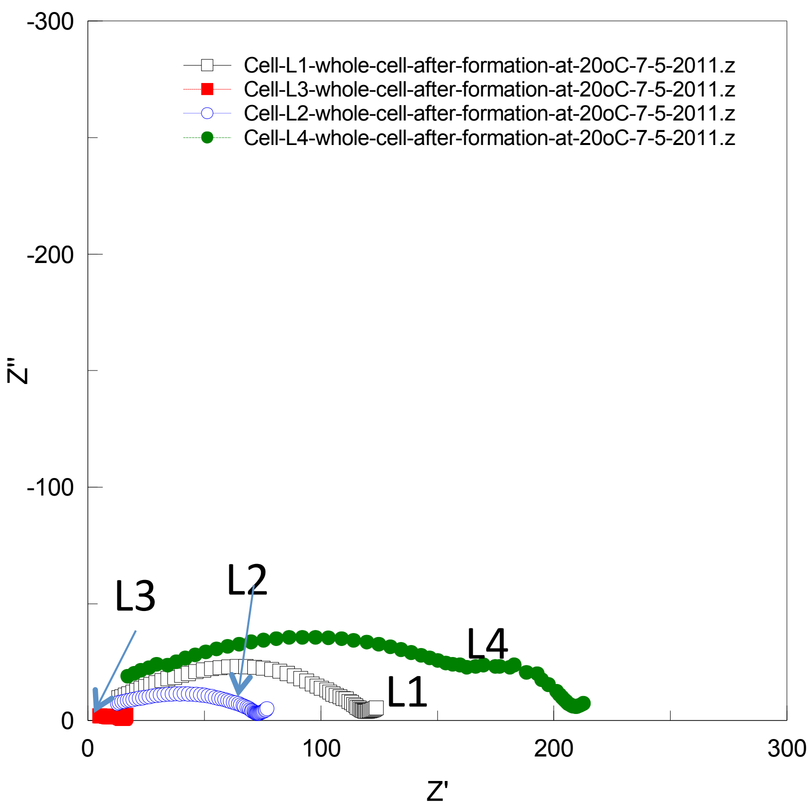
- Initial impedance: Group 3 << Group 2 < Group 1
- Implying inadequate electrolyte to wet electrodes or non-uniform electrolyte distribution in Group 2 and Group 1 (worse in Group 1)

Full Cell Pouch Cell Assessment: Formation Cycling Electrolyte Quantity Equivalent to Actual Cells



Formation capacity corresponds fairly well with the initial impedance measurement

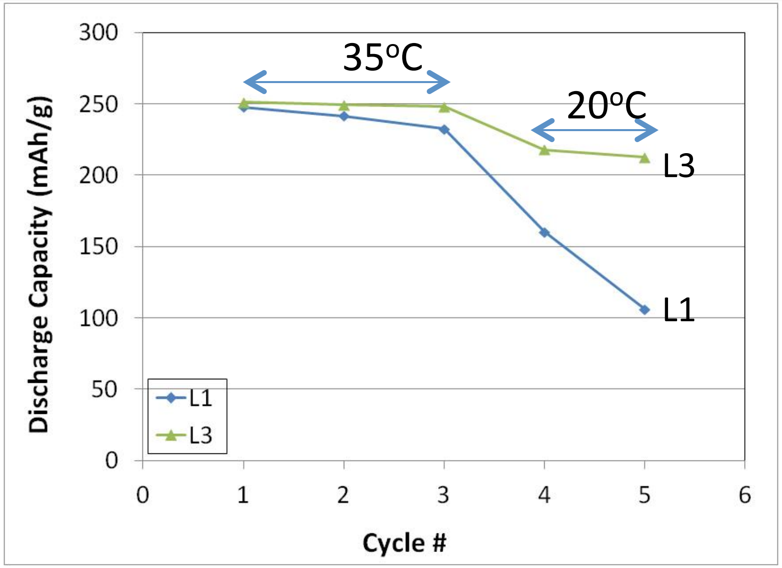
Impedance Measurement: After Formation Pouch Cells with Limited Electrolyte



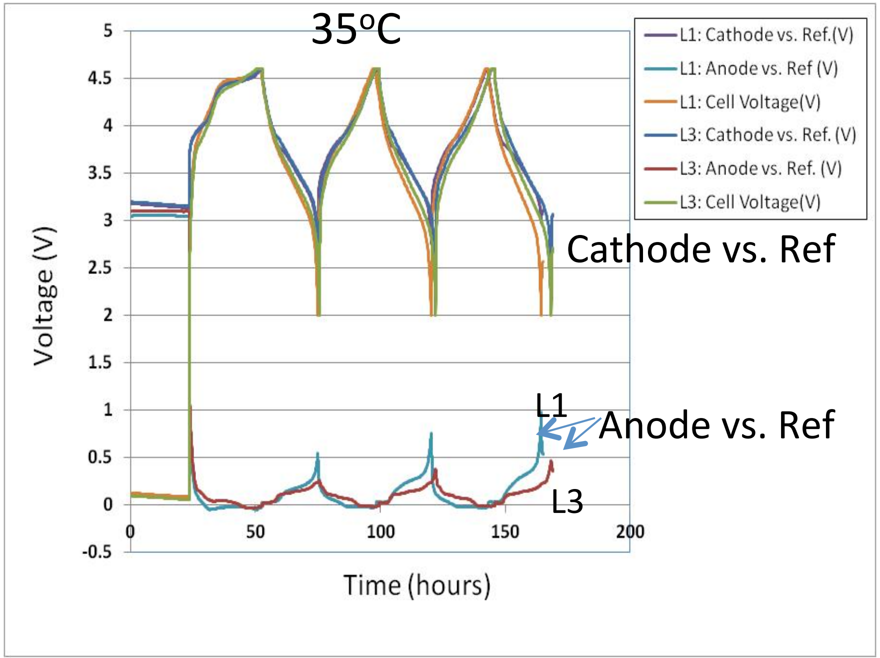
L1: Tonen, limited electrolyte
L2: Celgard, limited electrolyte
L3: Tonen, limited electrolyte
L4: Celgard, limited electrolyte

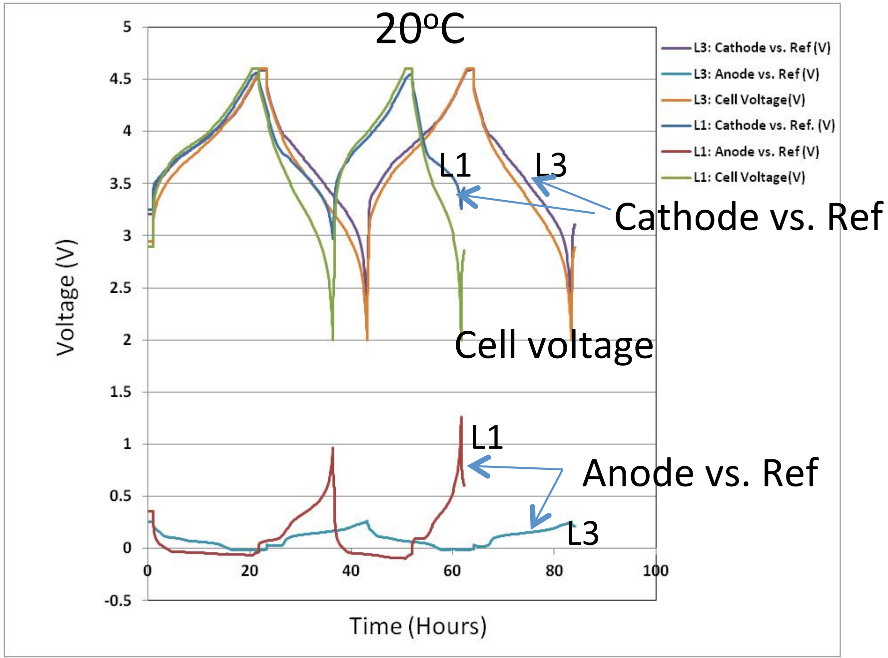
Poor formation discharge capacity has a corresponding higher cell impedance

Voltage Profile from Reference Electrode: Increase Anode Voltage Causes Fast Capacity Fade

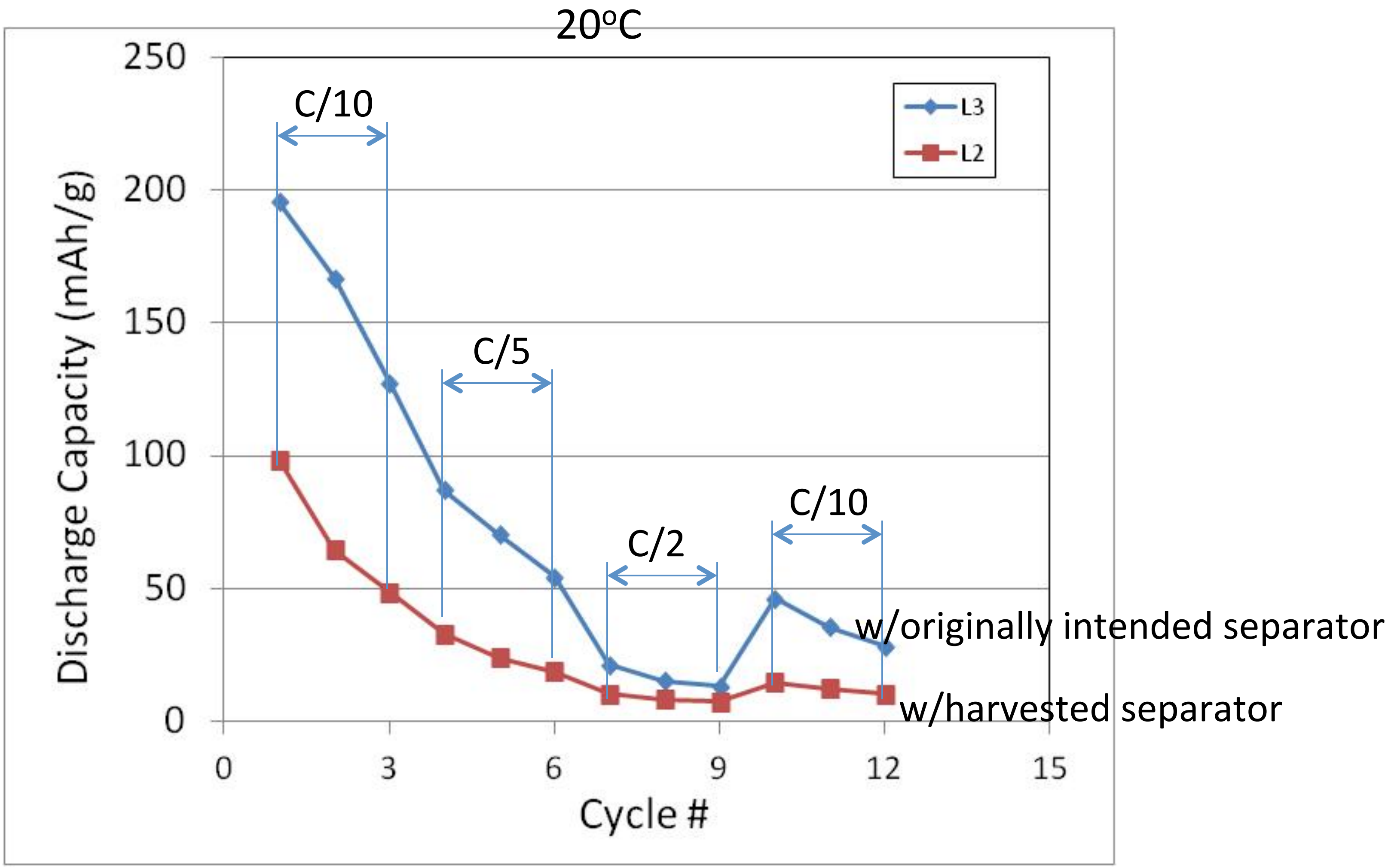


L1: Tonen, limited electrolyte
L3: Tonen, limited electrolyte





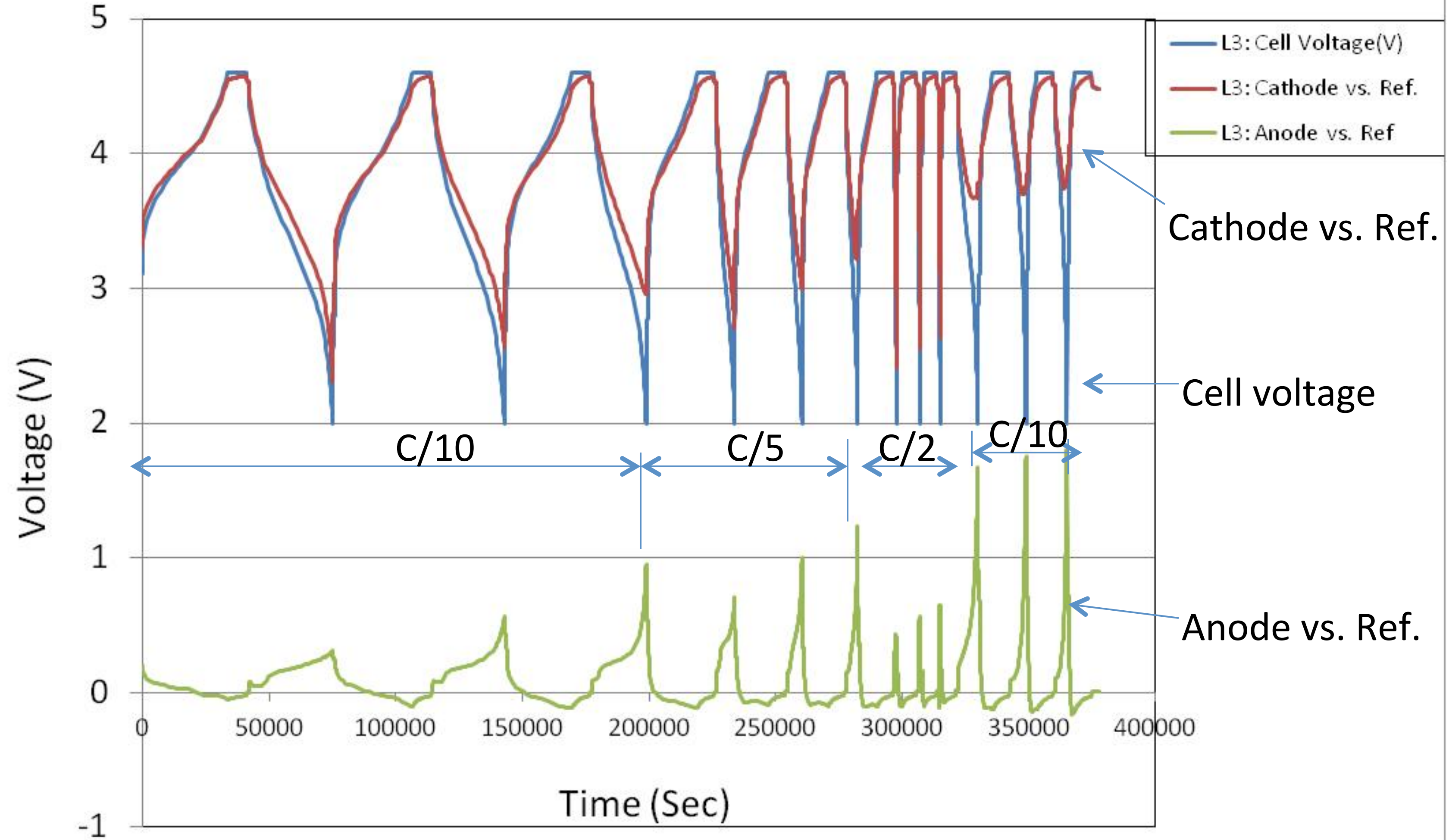
Rate Capability Cycling Test with Limited Electrolyte



Cells with limited electrolyte give poor rate capability cycling results
Worse w/harvested separator

Voltage Profile of Cell vs. Corresponding Individual Electrode

L3 (with originally intended separator)

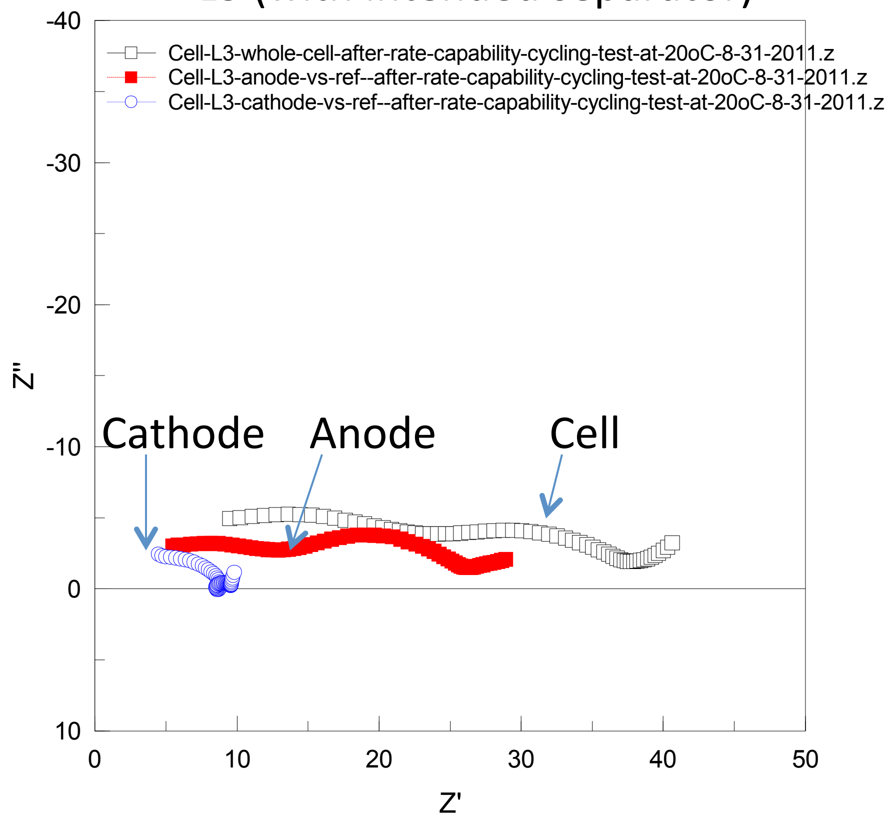


Rapid rising anode voltage causes cells to reach cut-off voltage earlier

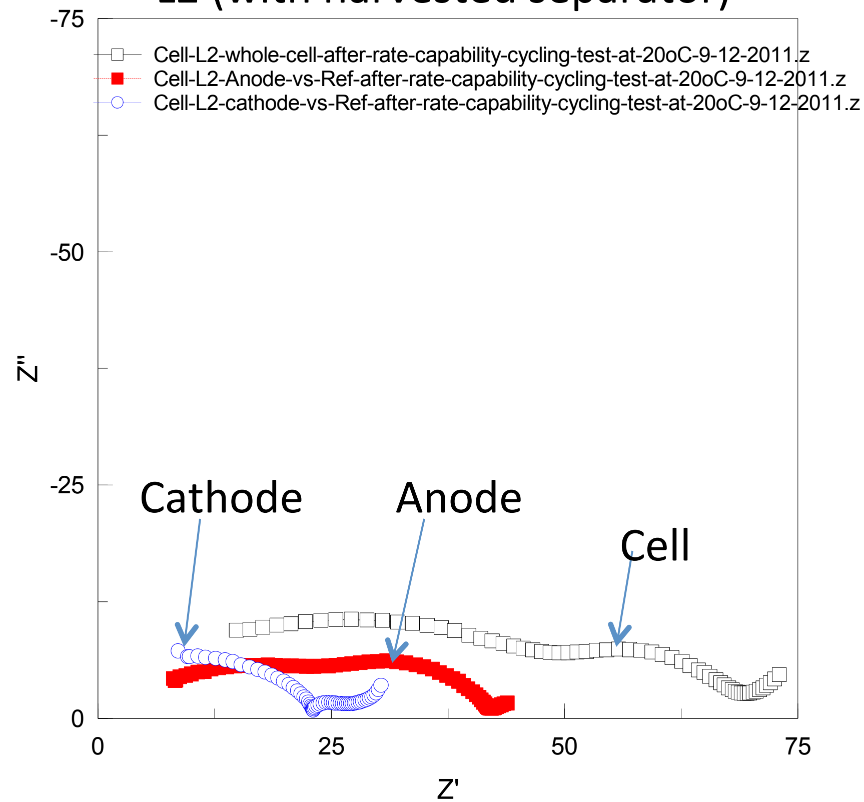
Impedance after Rate Capability Cycling with Limited Electrolyte

20°C

L3 (with intended separator)



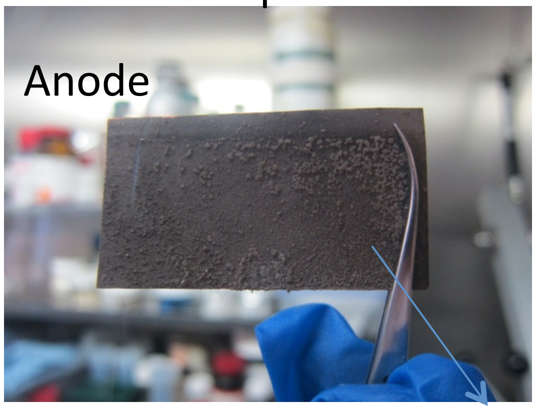
L2 (with harvested separator)

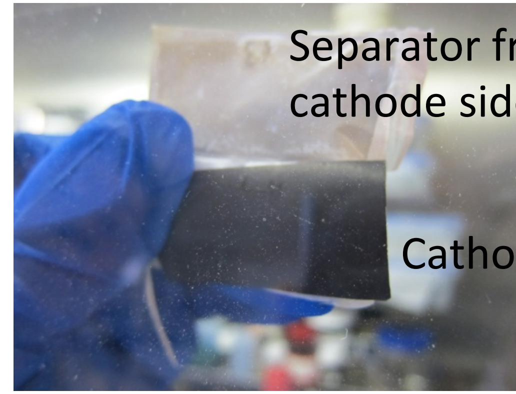


Anode impedance dominates in the cell impedance after rate capability cycling

Destructive Physical Analysis (DPA)

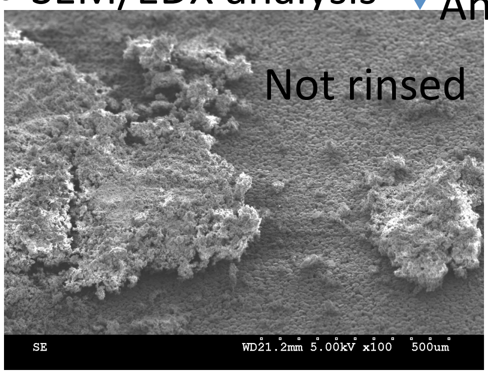
- The cell components were dry

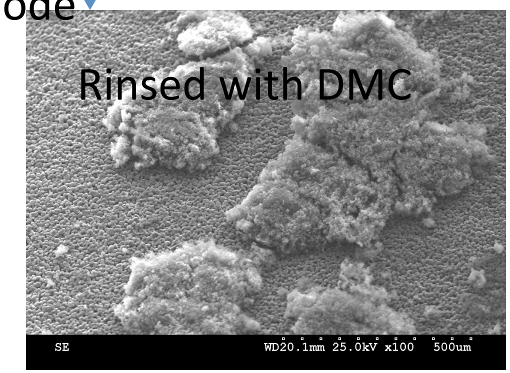




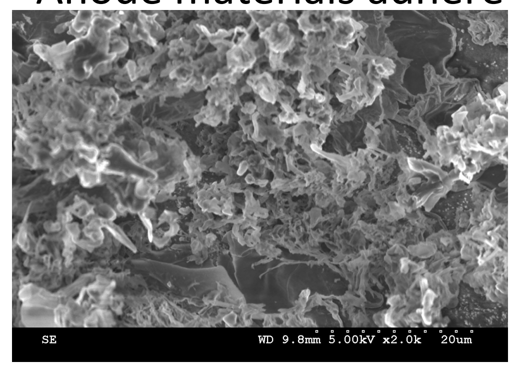
- SEM/EDX analysis

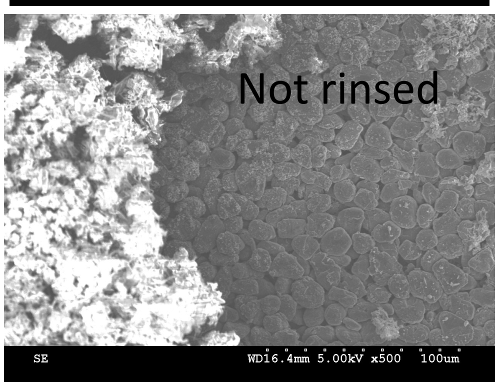
Anode

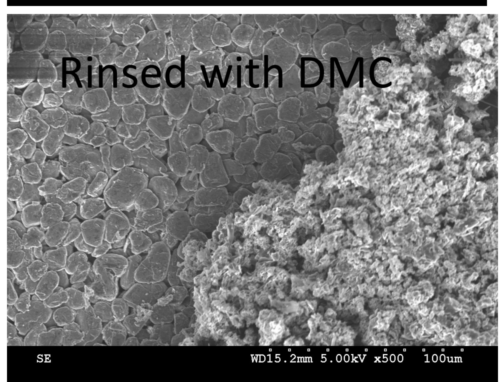




Anode materials adhere to separator

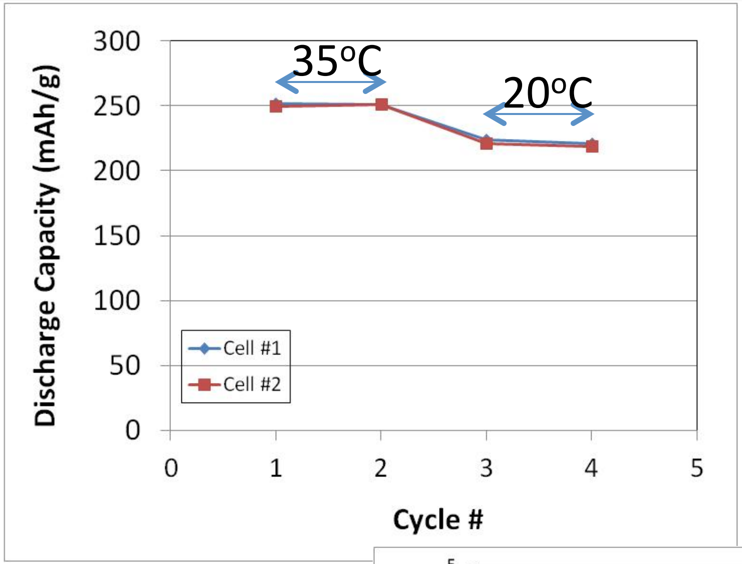


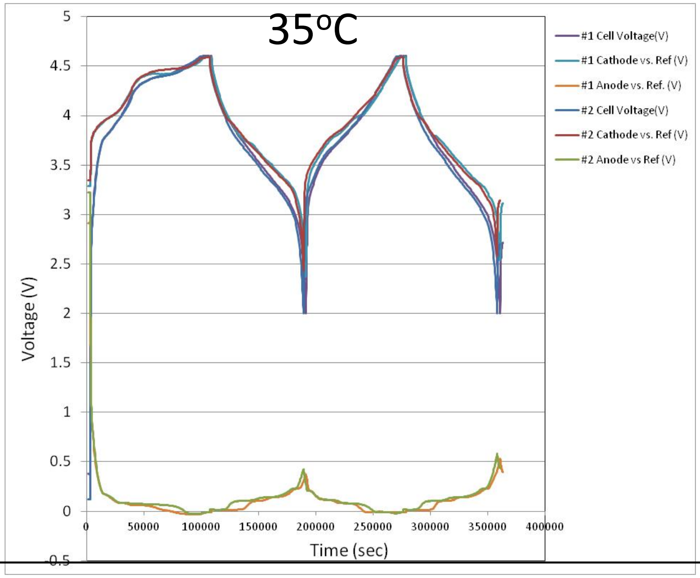


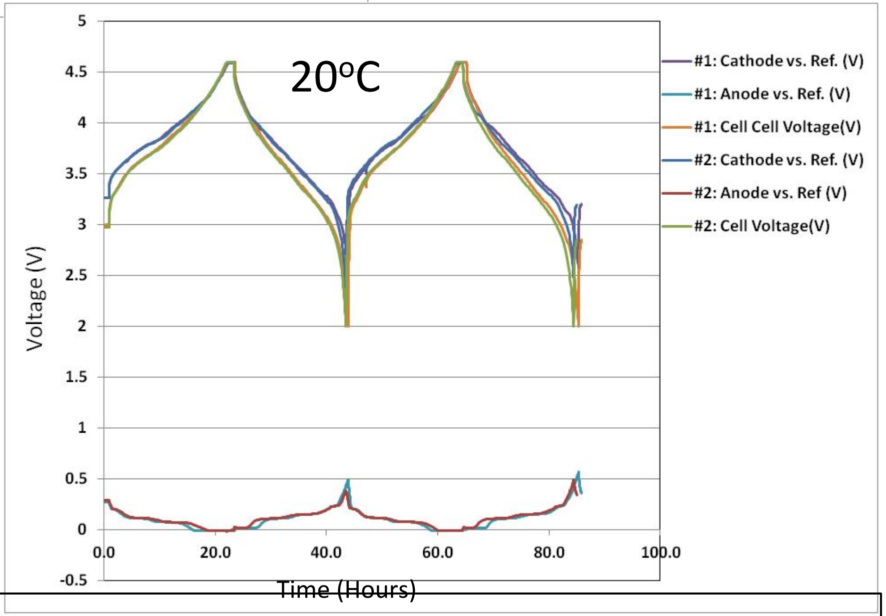


- The cell components were dry
- Elements such as Mn, Ni, Co, Cu were detected in EDX mapping
- Mn: dissolution from cathode and migration to the anode

Full Cell Pouch Cell Assessment: Formation with Flooded Electrolyte

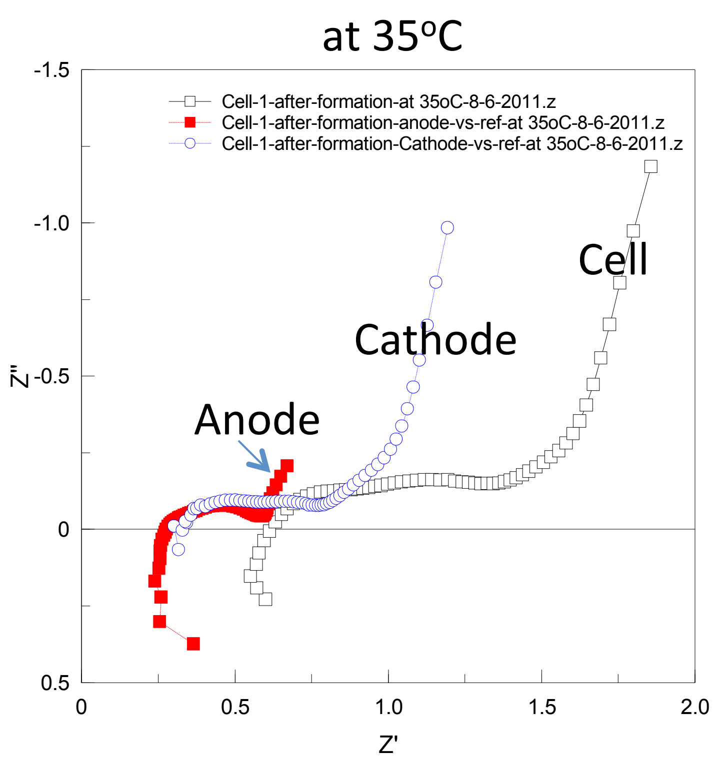


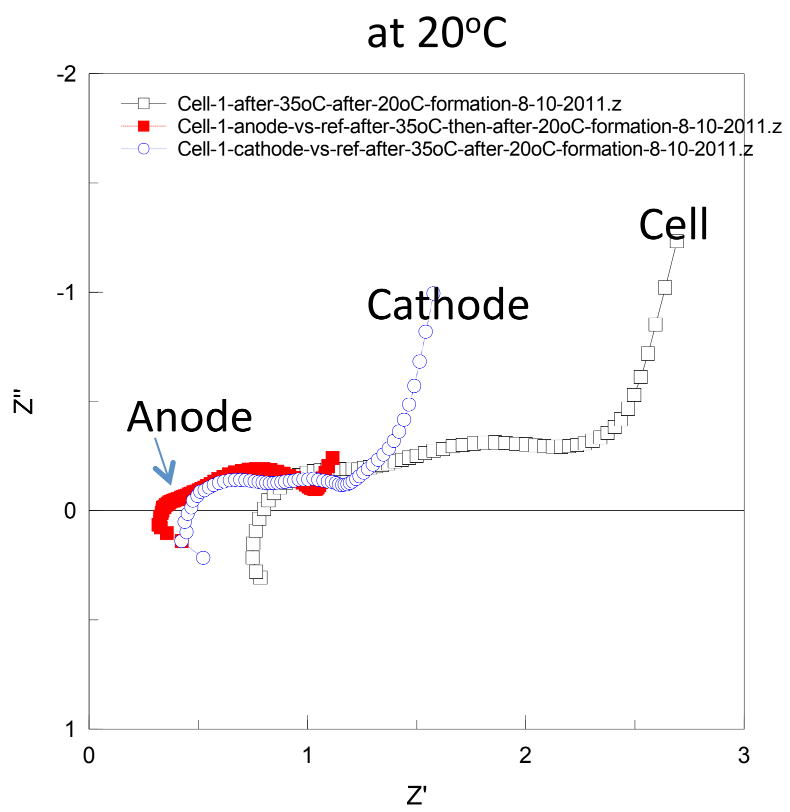




Consistent formation data (with minimum variation) with flooded electrolyte

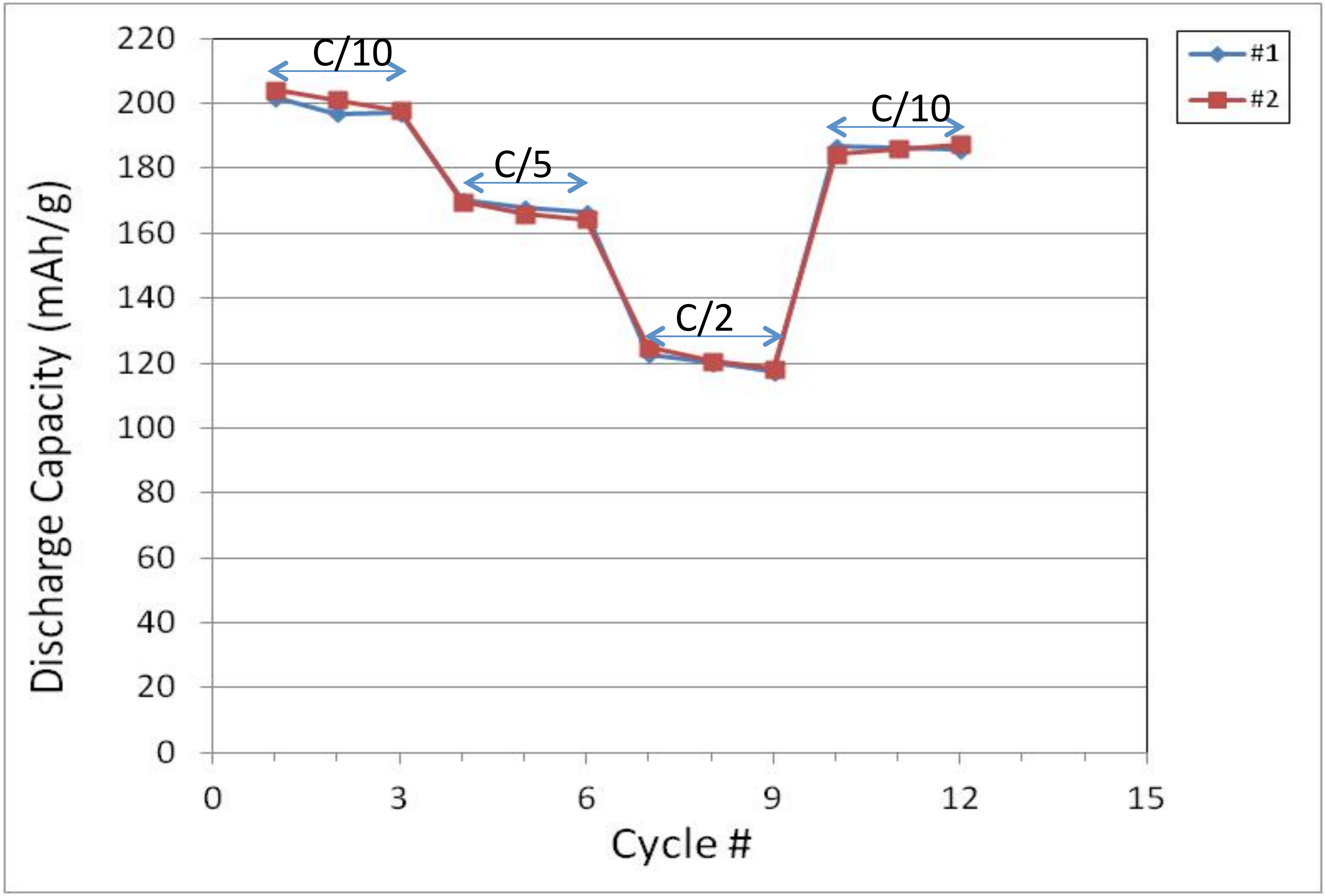
Impedance after Formation of Pouch Cell with Flooded Electrolyte





The cathode electrode dominates the diffusion part in the cell impedance

Rate Capability Cycling Test with Flooded Electrolyte

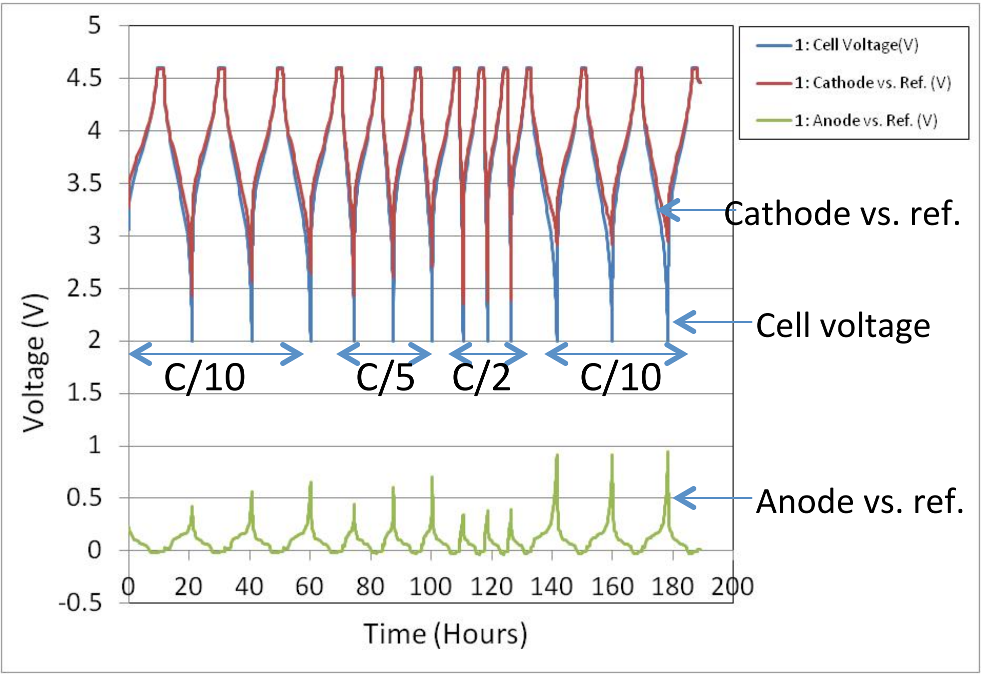


Consistent rate capability cycling data with flooded electrolyte (but appear to be sensitive to rate)

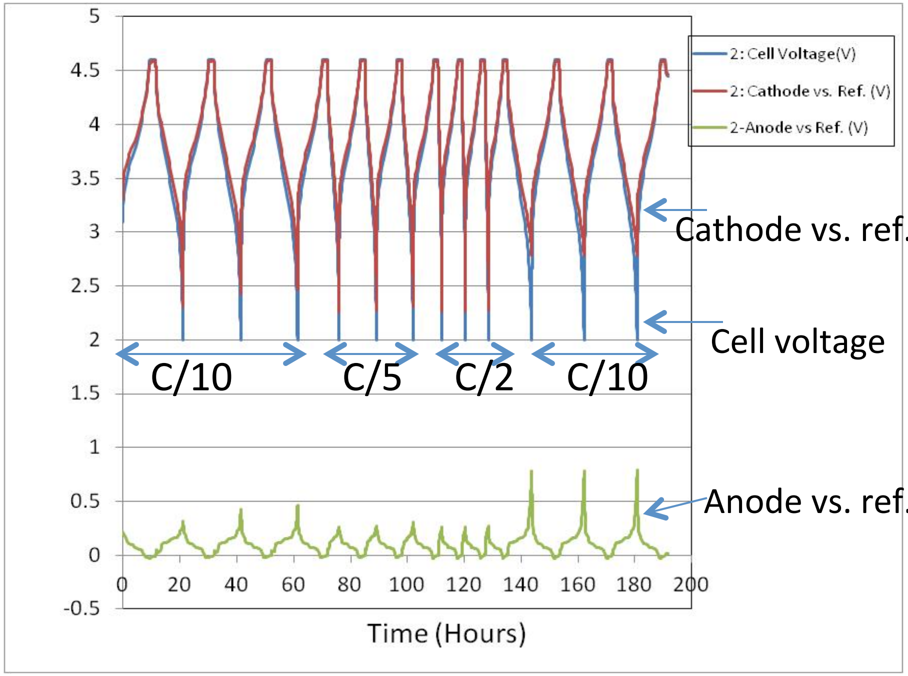
Voltage Profile of Cell vs. Corresponding Individual Electrode with Flooded Electrolyte

20°C

Cell #1



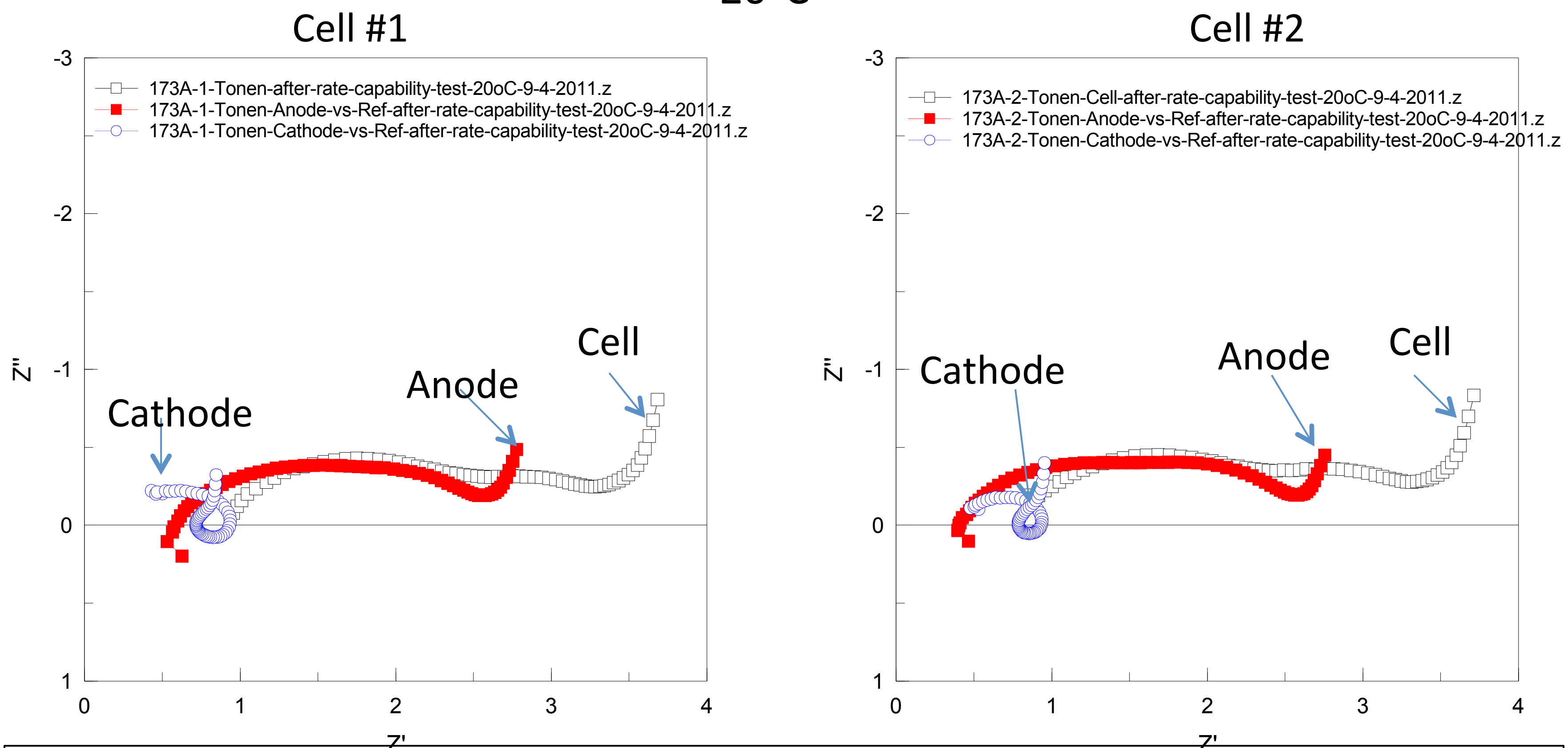
Cell #2



Consistent voltage profiles, and anode voltage profile becomes normal but could not recover at 2nd C/10 cycling

Impedance after Rate Capability Cycling with Flooded Electrolyte

20°C



- The cell internal resistances of the cell, anode and cathode remain the same before and after rate capability cycling
- The cell charge transfer resistance increases significantly, and is mainly from anode side

Lessons Learned - Summary

- The wrong separator was mistakenly used in the actual cell build, but it is only part of the reason for the poor capacity fade

- Inadequate electrolyte in the cells and/or non-uniform distribution of electrolyte are among the factors for the cell failure

- Inadequate electrolyte/non-uniform distribution has a significant impact on anode performance: incomplete anode wetting can cause Li plating, resulting in the anode voltage to rise rapidly (passivation) and forcing the cell to reach cut-off voltage earlier and the fast capacity fade

- The anode performance may worsen due to Mn dissolution from the cathode to dope/poison the SEI on anode surface, especially with limited electrolyte conditions

Recommendation/Next Step

- Cathode coating to reduce/eliminate the Mn dissolution
- Additives in electrolyte to minimize the Mn dissolution/migration to anode
- Allow to have adequate electrolyte in the cell

Acknowledgements

- Eunice Wong for SEM/EDX analysis
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Thank you!